On the physical basis for the nematic rubber elastic free energy

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We discuss why it is physical to keep terms in the nematic rubber elastic free energy that reflect the order parameter dependence of the natural size of the network polymers. We address a point of difficulty in some mathematical approaches to this problem.

I. INTRODUCTION

Nematic elastomers are formed by crosslinking nematic polymers. Such molecules order orientationally because of rod-like elements incorporated in their main chains (MC polymers) or pendant as side chains (SC). In both cases orientational order induces the backbones to change their mean shapes from spherical to elongated (prolate) or flattened (oblate) forms. Since chain shape and the macroscopic shape of a network are intimately related, there is a strong coupling between the nematic order and the shape of such solids. This obtains for both prolate and oblate chain shapes – our conclusions will hold for both types of polymer. Several elastic phenomena, unique to nematic elastomers, arise from this coupling. The most relevant in a discussion of changing the magnitude of the order Q, is that such changes induce huge elongations and contractions (of many 100s%). The order can be changed by changing temperature, or by illumination if at least some of the rods contain chromophores. The effect is reversible and is described in a monograph [1] that summarises the work of many research groups. The magnitude of the spontaneous elongation, λ_m, is proposed (as explained below) as an indicator of the shape anisotropy of the polymers, $\lambda_m = (\ell_\parallel/\ell_\perp)^{1/3}$, where $\ell_\parallel$ and $\ell_\perp$ are the Flory effective step lengths parallel and perpendicular to the nematic ordering direction, $\mathbf{n}$.

Our purpose here is to clarify the way in which, at constant temperature, the nematic can perhaps change the magnitude as well as the direction of its order as distortions are imposed. For instance, close to the nematic-isotropic transition, or in regions of extreme distortion close to the core of a disclination, Q may reduce. Some investigations, particularly from the mathematical community, have had understandable concerns that the standard nematic rubber elastic free energy apparently has terms unbounded from below in the limit $Q \to 1$. To retain a physical description, authors have instead rigidly constrained such terms to be constant. We point out that (i) realistic chain models do have the critical terms varying, and (ii) that there are more practical and physically-founded ways to deal with this apparent difficulty.

A simple extension[1] to nematic elastomers of the classical Gaussian theory of rubber elasticity yields a model, ideal free energy density:

$$f_{\rm el} = \tfrac{1}{2}\mu \left[\mathrm{Tr}\left[\underline{\underline{\ell}}_0 \cdot \underline{\underline{\lambda}}^{\rm T} \cdot \underline{\underline{\ell}}_{\mathbf{n}}^{-1} \cdot \underline{\underline{\lambda}} \right] + \ln\left(\frac{\mathrm{Det}[\underline{\underline{\ell}}_0]}{\mathrm{Det}[\underline{\underline{\ell}}]} \right) \right] \quad (1)$$

where μ is the shear modulus of the rubber in the isotropic state. $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}_{\mathbf{n}}$ are the Flory effective step length tensors that give the mean square dimensions of a nematic Gaussian polymer, and there characterise the distribution of chain shapes. The former is at formation and the latter is that currently pertaining, that is after any director rotation or changes in Q induced by strain, or due to temperature or illumination change. Thus:

$$\langle R_\parallel R_\parallel \rangle = \frac{1}{3}\ell_\parallel L, \quad \langle R_\perp R_\perp \rangle = \frac{1}{3}\ell_\perp L, \quad (2)$$

with $\ell_\parallel$ and $\ell_\perp$ the effective step lengths along and and perpendicular to the director, and where L is the chemical arc length of the polymer. $\underline{\underline{\ell}}_0$ and $\underline{\underline{\ell}}_{\mathbf{n}}$ depend on the order at formation and that currently pertaining (Q). The deformation gradient tensor is $\underline{\underline{\lambda}}$ and takes the body from its formation state to that current. Since rubber is a soft solid, deformations are strictly at constant volume and thus $\mathrm{Det}[\underline{\underline{\lambda}}^{\rm r}] = 1$. Such a description of the network chains presumes they are long enough to be Gaussian, albeit anisotropic. It is reasonable to make this restriction for otherwise chains would not be dominated by their random configurations and nor would they be so highly extensible as their experimental response clearly demands. With this generic assumption, it then does not matter greatly what kind of model one adopts for chains – the Flory philosophy is that local molecular structure is washed out by randomness and can be encoded by ℓ (here two numbers $\ell_\parallel$ and $\ell_\perp$). The simplest model is that of the freely jointed chain with links of length a whereupon orientational order induces:

$$\frac{\ell_\parallel}{a} = (1+2Q), \ \frac{\ell_\perp}{a} = (1-Q), \ \frac{\mathrm{Det}[\underline{\underline{\ell}}]}{a^3} = (1+2Q)(1-Q)^2 \quad (3)$$

For elastomers over a large range of order parameters and hence also extensions the freely jointed chain model has proven highly accurate. It is found [3] that spontaneous deformations arising from eqn (1), $\lambda_m = ((1 + 2Q)/(1 - Q))^{1/3}$ correlates perfectly with independent measurements of Q from optical anisotropy which,

along with λ_m varies as temperature is changed. Here, distortions λ_m are with respect to a high temperature reference state where $Q \to 0$ and $\lambda_m \to 1$. Chains can be highly extended by high nematic order, attaining for instance a hairpin state which has a much more rapid increase of $\ell_\parallel$ with Q and hence with T [4]. In any event the picture of the effective step lengths and hence $\text{Det}[\underline{\ell}]$ varying with Q persists for all known chain models. It is unphysical to constrain the determinant to a fixed value. A supplementary argument that has been advanced for the fixing of $\text{Det}[\underline{\ell}]$ is that this is effectively proportional to the volume in spaced covered by the chain and that chains are incompressible, i.e. the $\text{Det}[\underline{\ell}]$ cannot change. The expression refers to the extent of the chain, a volume proportional to $N^{3/2}$ since it is a random walk of lineal dimension proportional to $n^{1/2}$. The actual volume occupied by the monomers of the chain scales like N (times a^3) and thus the density of segments of a particular chain is $\sim N^{-1/2}a^{-3}$ – chains are very dilute in a melt and most of the space they span is occupied by other chains. There is accordingly no volume constraint presented to a given chain. In fact this argument is at the heart of why chains adopt ideal statistics in a melt [5].

What then stops the free energy density (1) minimising at $f = -\infty$ by tending to $Q = 1$ where $\text{Det}[\underline{\ell}] = 0$ and hence $\ln\left(\text{Det}[\underline{\ell}_0]/\text{Det}[\underline{\ell}]\right) \to -\infty$? One must consider the dominant free energy in the problem, namely that of the underlying nematic phase rather than the weaker rubber part. The nematic chains have, in the absence of linking, a nematic free energy density $f_N(Q)$ that one can show to be additive to the rubber part arising on linkage. Model forms arise from simple Landau-de Gennes phenomenology, or from particular molecular models, for instance the extension of Maier-Saupe nematic theory to worm-like chains. In fact a freely jointed rod model of nematic chains [6] would have exactly the Maier-Saupe nematic free energy since the rods are independent, except through their nematic interactions. As with the chains, it is not vital for our argument what model one adopts. They all have in common a free energy of order $k_B T_{ni}$ *per monomer* where T_{ni} is a characteristic temperature where nematic order is lost. The rubber free energy by contrast is of the order of $k_B T$ per network strand since the prefactor in the free energy density eqn (1) is the modulus $\mu = n_s k_B T$ where n_s is the number density of strands. Thus the rubber component of the free energy density is of order $1/N$ smaller than the nematic part. N is the number of effective step lengths separating crosslink points along a chain. N has to be large, $\sim 10 - -100$ in order that chains are Gaussian and the network is rub-

bery, that is highly extensible and dominated by entropy. The overall dependence of the free energy on Q is dominated by the minimum determining the stable state of the liquid under the same conditions. It is little perturbed by the Q-dependent terms arising from the rubber, including the $\ln\text{Det}[\dots]$ term. The rubber adds terms like $\frac{1}{N}(-Q_0^2 Q^2 + Q^4)$ [1, 6, 7] for the ideal case and where spontaneous extension/contraction has been allowed to occur. (Q_0 is the order at crosslinking.) These terms cause minor shifts in the transition temperature and latent heat. In the non-ideal case, involving memory of orientation pertaining at formation, a term like $-\frac{1}{N}Q$ arises, which resembles the form of an external field and removes the isotropic high temperature phase Q identically equal to zero altogether.

Strictly speaking, even though the liquid nematic free energy dominates the nematic contributions from the rubber, the $\ln\text{Det}[\dots]$ term would still yield a separate minimum at $Q = 1$. However the use of the result $\ell_\perp = a(1 - Q)$ near the point $Q = 1$ is also unphysical. This limit of perfect orientational order would suggest that $\langle R_\perp^2\rangle \to 0$. Only for chains mathematically narrow and without any directional fluctuations (at $T = 0$) could attain this limit. In any case the Gaussian approximation of this result will also have long since failed.

How should one proceed? Physically, one is constrained to being near in Q to a modified nematic minimum in the free energy. One can thus reasonably ignore any minimum near $Q = 1$ and rely on the nematic free energy to naturally constrain Q-dependence arising in f_{el}. Practically, unless one is close to the N-I transition where the minimum in f near $Q = 0$ is not stiff, one can take Q to be fixed in magnitude. If strains are extreme, then one can let Q have the freedom to respond to perturbations arising from $f_{el}(\underline{\underline{\lambda}}, Q)$ by taking the nematic free energy to be $\frac{1}{2}f_Q'' \cdot (Q - Q_{\min})^2$ (with f_Q'' the curvature of the potential at $Q_{\min}$), which was an approached followed in [3]. These authors were concerned changes in the linear modulus from applied strains inducing changes in Q. This work also considered the role of $\underline{\underline{\lambda}}$ in inducing changes in the biaxial order if the principal stretch direction was not aligned with $\mathbf{n}_0$. Such changes too must be accounted for in the changing $\ln\text{Det}[\dots]$ term that is the subject of this note.

In summary we have argued physically as to why another source of Q-dependent free energy terms from rubber elasticity must not be constrained to take a constant value. In fact their form relates closely to well tested models of chain statistics and for the Gaussian theory of nematic rubber elasticity to hold, these terms must be retained.

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